AN INVESTIGATION OF THREE ZINC BORATE SYSTEMS

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CHAPTER I

INTRODUCTION

Varying ratios of zinc and boron are known to exist in the form of zinc borates. These borates may be bonded to varying numbers of water molecules. The purpose of this study was to examine three of these hydrated forms which have been obtained from a commercial laboratory in an attempt to determine their composition and to determine the number of water molecules associated with each commercial borate.

Boron is the fifth element of the periodic table. In the form of borax ($Na_2B_4O_7 \cdot 10H_2O$) it has been a product of industry for hundreds of years. The element itself is difficult to isolate and many of its earlier assigned characteristics by early investigators are now known to refer to a highly impure oxygen containing material.

The best known compounds of boron are derivatives of boric acid, H_3BO_3, and its anhydride, B_2O_3.

Borates are understood to be those molecules characterized by a combination of a metal oxide, boron oxide, and usually one or more water molecules. Several borates have been investigated, but the zinc borates have probably been studied the least of all known borates. A reason for this disparity is that zinc borates can theoretically have a

multitude of combinations of zinc, boron, oxygen, and hydrogen. Thus the possible structures of zinc borates are many.

Also, zinc borates have been relatively unimportant in commercial circles until the last twelve to fifteen years. Recently, zinc borates have been found to be a valuable ingredient in fire retardant systems for such varied commercial products as natural rubber, textiles such as burlap, window shades, and various paints. The explanation for the fire preventative property is that the zinc borates lose water of hydration as steam which helps snuff out flames.

It was the initial hope of this paper that structures of the three zinc borates under investigation might be given definite assignments. However, it was soon realized that any suggestions regarding molecular structure had to be made with reservation.

I. NOMENCLATURE

Various ions mentioned in this paper have the form; BO_3^{-3}, $B_2O_5^{-4}$, and $(BO_2)_n^{-n}$. These forms were occasionally referred to as the orthoborate, pyroborate, and metaborate anions respectively.

II. HISTORICAL RESUME

D. H. Kabakjian[1] in 1936 studied various luminescent zinc borate compounds which could be obtained in either vitreous or crystalline form. Kabakjian investigated the dependence of luminescence of various compounds on their physical structure. He found that zinc borate compounds can be made luminescent without the addition of any activator.

He mixed a proportion of zinc and boric acid corresponding to the formula ZnB_2O_4 and heated the preparation to a temperature of approximately 500°C to form an amorphous mass. Fusion of this mass occurred near 1000°C to form a clear zinc borate glass. He further subjected the "pure" zinc borate to a cathode-ray spectrogram analysis and obtained a maximum emission at about 4000 A°.

Ingerson, Morey, and Tuttle[2] in 1948 made melting point determinations in the system $ZnO \cdot B_2O_3$. They determined the melting points for zinc oxide weight per cents ranging from 47.2 per cent to 77.2 per cent. It was assumed that the melting point of the above system was 1000°C. An examination was also made of a phase study of the system

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[1]D. H. Kabakjian, "Dependence of Luminescence on Physical Structure in Zinc Borate Compounds," Physical Review, LI (March, 1937), 365-368.

[2]Earl Ingerson et al., "The Systems K_2O-ZnO-SiO_2, ZnO-B_2O_3-SiO_3," American Journal of Science, XXXI (April, 1948), 237.

$5ZnO \cdot B_2O_3$ and $ZnO \cdot B_2O_3$.

Edwards, Morrison, Ross, and Schultz[1] in 1955 investigated the structure of various aqueous borate ions with the infrared spectrum of a powdered sample of teeplite which contained the structure $H_2BO_3^-$. This showed only absorption in the region of 900-1000 $cm.^{-1}$. However, it was believed that a band for a tetrahedral structure could be assigned at 941 $cm.^{-1}$ according to specific selection rules. The synthetic teeplite was prepared by mixing equal volumes of saturated solutions of sodium chloride and sodium borate.

Of considerable interest was the work done in 1956 by Harrison and Hummel.[2] A phase relationship was established in the system containing zinc oxide and boric oxide. It was claimed that two compounds existed; $5ZnO \cdot 2B_2O_3$ and $ZnO \cdot B_2O_3$. Both compounds exhibited low and high polymorphic forms.

Further examination revealed (α)$ZnO \cdot B_2O_3$ to invert somewhat sluggishly to the high temperature (β)$ZnO \cdot B_2O_3$ at 600°C and very rapidly at 900°C. The melting point was determined to be 982°C.

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[1]John O. Edwards et al., "The Structure of the Aqueous Borate Ion," Journal of American Chemical Society, LXXVII (January, 1955), 266-268.

[2]D. E. Harrison and F. A. Hummel, "Phase Equilibria and Fluorescence in the System Zinc Oxide-Boric Oxide," Journal of the Electrochemical Society, CIII (September, 1956), 491-498.

It was also determined that the $3ZnO \cdot 2B_2O_3$ compound was the only zinc borate, glassy or crystalline, insoluble in acid. Melting points of 1000°C and 1080°C were assigned to $ZnO \cdot B_2O_3$ and to $5ZnO \cdot 2B_2O_3$ respectively.

A direct relationship between refractive index to an accuracy of ±0.002 and per cent composition of zinc borates was introduced. It was also found that at concentrations of zinc oxide above 70 per cent in any zinc borate made it impossible for the borate to recrystallize after melting into a glass.

Differential thermal analysis data was obtained for the 3:2, 1:1, and 1:2 composition of ZnO to the borate anion which had previously been heated to 800°C. A sharp endothermic peak was observed at 900°C and thought to be due to conversion of a low temperature form of $ZnO \cdot B_2O_3$ to the cubic high temperature form.

The product of 1:1 and 1:2 compositions of the above form after differential thermal analysis was shown by X-ray data to be cubic $ZnO \cdot B_2O_3$. Ignition losses for the 1:1 and 5:2 compositions of the above form was found to be 27.58 per cent and 17.83 per cent respectively. Calculated weight losses for these were previously estimated to be 27.07 per cent and 17.51 per cent.

Steele and Decius[1] in 1956 made infrared absorption studies of indium borate and attempted calculations of force constants for the borate ion.

Krogh-Moe[2] in 1958 did an analysis in the infrared spectra region of various vitreous and crystalline borates. It was indicated that various authors have studied glass structures by infrared absorption spectra. Such studies have often been based on an assigning of peaks to definite structural components like BO_4, BO_3, and SiO_4 groups. However, warnings against an analysis of this type have appeared.

It was also indicated that structures like the BO_4 tetrahedra and BO_3 triangles in a glass will generally be strongly coupled with the surroundings. It was further asserted that these units are usually connected to a three dimensional network and a specific region of this network is characterized by infrared spectra.

A comparison of peaks in a glass compared to a crystalline structure was illustrated. The potassium bromide disc technique was used in the analysis.

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[1] W. C. Steel. "Infrared Absorption of Lanthanum, Scandium and Indium Borate and the Force Constants of Borate Ions," Journal of Chemical Physics, XXV (December, 1956), 1184-1188.

[2] J. Krogh-Moe, "The Infrared Spectra of Some Vitreous and Crystalline Borates," Arkiv for Kemi, XII (February, 1958), 475-479.

Parsons and Milberg[1] in 1959 investigated vibrational spectra of vitreous $B_2O_3 \cdot H_2O$ compounds. It was shown that the glass spectra were consistant with a random network structure in which each boron was triangularly coordinated by three oxygen atoms and that the presence of water leads to weak hydrogen bonds between oxygen atoms. No evidence was found for any substantial amount of tetrahedral coordination of boron by oxygen of either low or high water content.

Hart and Smallwood[2] in 1962 made an examination of borate anions with infrared techniques. Identification of the orthoborate ion has been possible in a number of compounds and some force constants were calculated. The pyroborate ion was found in other compounds, however frequencies were not assigned. Suggested structural arrangements for various borate groupings were indicated. It was indicated that the structure of the pyroborate zinc borate remained uncertain.

It was found that more clearly resolved spectra did not materialize as the specimens were cooled.

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[1]J. L. Parsons and M. E. Milberg, "Vibrational Spectra of Vitreous $B_2O_3 \cdot xH_2O$," Journal of The American Ceramic Society, XLIII (June, 1960), 326-330.

[2]P. B. Hart and S. E. Smallwood, "An Examination of the Infrared Spectra of Borate Anions," Journal of Inorganic Nuclear Chemistry, XXIV (December, 1962), 1047.

Buerger, Laves, Menzer, and Stranski[1] did an infrared spectra and structure analysis on some anhydrous zinc borates in 1962. The spectra indicated that all boron atoms are fourfold coordinated by oxygen in the crystalline modification and that a coordination change occurs during the fusion process. The stability of a borate network with tetrahedral coordinated boron atoms was briefly discussed with reference given to the boron-oxygen bond angle.

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[1] M. J. Buerger, "The Infrared Spectra and the Structure of Some Anhydrous Zinc Borates," Zeitschrift fur Kristallographie, CXVII (August, 1962), 166-170.

CHAPTER II

METHODS OF RESEARCH

The zinc borates which were obtained from a commercial laboratory were known to contain water of hydration. Furthermore, the manufacturer stated in his analysis that the borates were non-hygroscopic.

I. THERMAL ANALYSIS

Weight loss versus temperature. To determine the amount of hydration associated with each borate sample, it was necessary to construct an instrument for thermal analysis. An oven with an attached selective thermocouple control was employed. The oven was equipped with a pyrometer and any temperature could be selected and held for an indefinite period of time (See Figure 1).

An analytical balance was placed above the oven and a glass telescoping rod connected the weighing pan to a crucible harness. The crucible was allowed to hang half-way into the cylindrical oven chamber. The oven was covered with an asbestos plug which had a hole approximately 8 millimeters in diameter to allow the glass rod to swing easily.

Using the thermal equipment, each oven dried sample was examined for per cent weight loss at selected temperatures. Each temperature was held until the balance came to

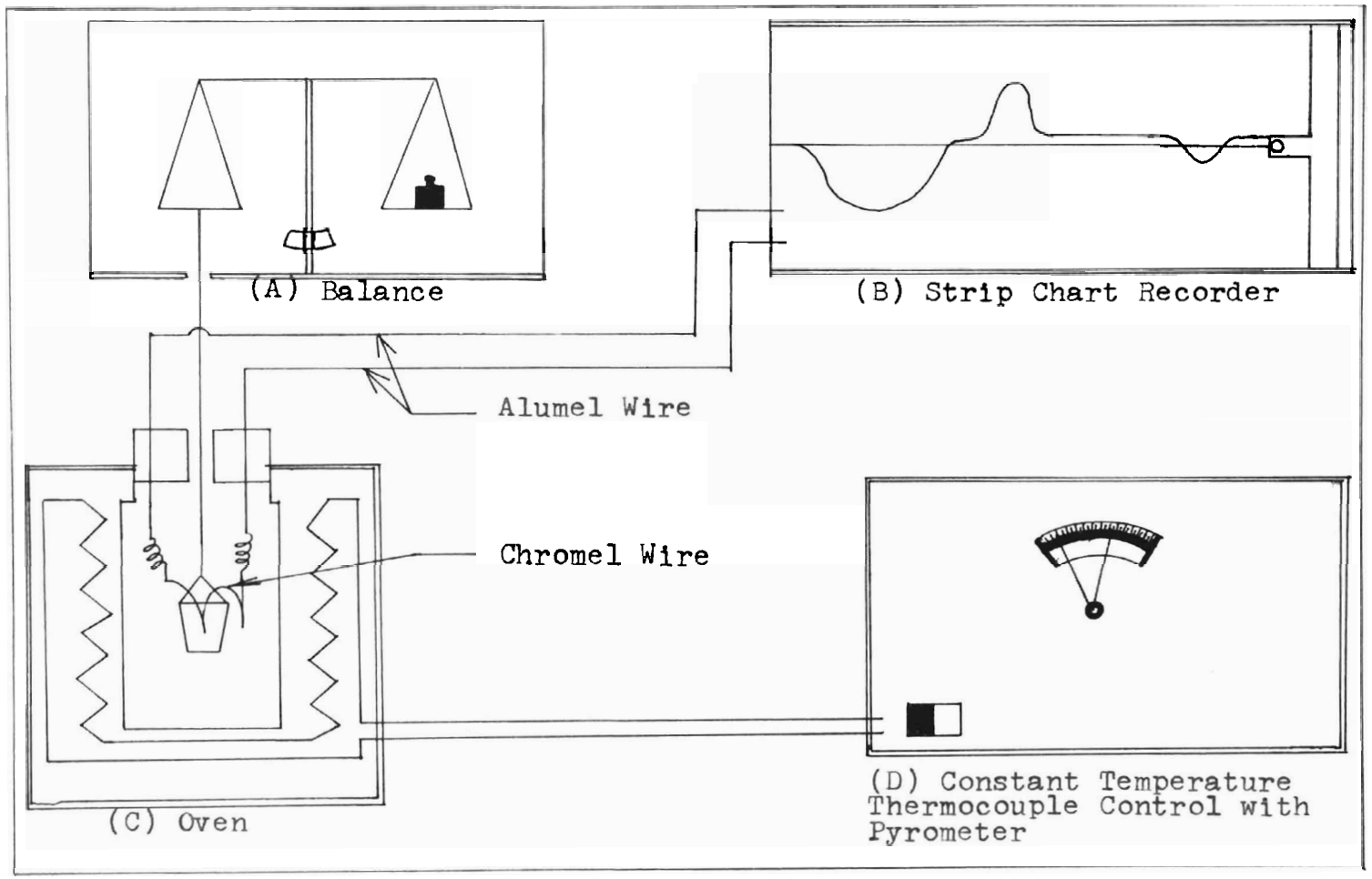

Figure 1. Instrument(s) for Thermal Analysis.

equilibrium. The purpose of this part of the study was to determine, from a graph of temperature versus weight loss, the number of water molecules which were coming off. The number of steps on such a graph would be indicative of the number of molecules of water.

Weight loss versus time. It was soon realized that such an analysis could be misleading because the corner of each "step" might be plotted which would give the appearance of a continual discharge of water molecules proportional to the oven temperature.

As a cross check for the weight loss versus temperature procedure, the oven dried samples were analyzed by recording weight losses at constant time intervals as the oven's temperature was increased at a uniform rate. To achieve the uniform rate, the pyrometer controls were turned to the maximum temperature setting possible and the oven's temperature increased at nearly a constant rate. A slower heat-up rate was noticeable only at high temperatures beyond the range of the analysis.

The above two procedures also gave values for loss on ignition for each oven dried sample. Loss on ignition for non-oven dried samples completed this phase of the thermal analysis.

Single thermocouple analysis. A strip chart recorder was combined with the above thermal equipment for thermocouple analysis. A chromel-alumel thermocouple was initially employed to analyze the samples at temperatures ranging from room temperature to temperatures in excess of 1000°C.

Because of the large temperature change, the samples, using a single thermocouple, were analyzed for relatively narrow temperature ranges. Larger temperature ranges were possible, but only if the amplitude of the potential difference was diminished. To overcome these limitations, differential thermal analysis was employed.

Differential thermal analysis. Two adjoining thermocouples were placed inside the oven (See Figure 1). One thermocouple was placed in the sample which was in a porcelain crucible and the other was kept in the sample's oven environment. Thus, a difference in potential was only achieved when the temperature inside the crucible differed from the environmental temperature. This type of analysis allowed the samples to be continually investigated for temperatures ranging from room temperature to temperatures in excess of the sample's melting point. Also, the amplitude produced by the difference in potential could be selected at will.

II. INFRARED ANALYSIS

All of the spectrophotometer analyses on borates which were found during the literature research were examined in the infrared range.

The borates were analyzed using very dilute proportions which were prepared in tightly compressed potassium bromide discs that could be placed in the spectrophotometer's light beam.

The samples were investigated to determine similarities in absorption frequencies at various critical sample states as determined from the differential thermal analysis. Infrared data was also used to classify the borates as a specific type of zinc borate. Two extra artificial mixtures of this type of borate were prepared and analyzed in the infrared range. In previous studies infrared analysis has also been used to determine the structure of various borates. Absorption peaks at specific frequencies indicated possible structural units present. The infrared range was also used to examine water of hydration which appeared at definite absorption frequencies.

III. PER CENT COMPOSITION ANALYSIS

From the infrared data the borates were inferred to belong to a definite type of zinc borate. The borates were

melted and allowed to solidify into a clear glass. Previous analyses have revealed that the refractive index increases directly with the per cent weight composition of zinc oxide in a zinc borate.

The glasses were cut with a circular diamond saw to a dimension which could be used in an Abbe Refractometer. After cutting, the glasses were ground with a glass grinding wheel and then polished with aluminum oxide. The indexes of refraction were found and the per cent composition of the borates were to be taken from a previously constructed graph of per cent weight composition versus refractive index.

CHAPTER III

STANDARDIZATION OF EQUIPMENT

Introduction. The oven, which was schematically illustrated in Figure 1, was warmed up and the pyrometer was checked against several thermometers. The pyrometer was shown to be in considerable disagreement with the temperatures as registered by the various thermometers. An attempt was made to adjust the electronic equipment associated with the oven's thermocouple, but no satisfactory equilibrium could be established. Therefore, a calibration curve for the pyrometer was constructed.

The balance, which was schematically illustrated in Figure 1, had to be placed directly over the oven as dictated from the experimental design of the equipment. Although the hole in the oven's plug was small as was the hole in the balance, it was considered necessary to check for the possible need of baffles between the balance and the oven. This was established by determining a zero point reading as a function of temperature of the oven.

The thermometers used in the study were used to determine the oven's actual temperature at low temperatures. A correction for the fraction of the stem emersion of the thermometer was computed.

Pyrometer standardization. The oven used in the study was a heavy duty Lindberg oven with a # 2 Platinel Thermocouple.

Actual oven temperatures between room temperature and 275°C were obtained with thermometers. Above 275°C three points were plotted corresponding to the melting points of lead, zinc, and silver. The melting points for the three elements are 327.5°C, 419.4°C, and 960.8°C respectively. The melting points were plotted in Figure 2.

The oven was constantly higher in temperature than the pyrometer indicated. Above 250°C the oven's temperature was uniformly related to the indicated pyrometer temperature as is indicated by Figure 2.

Thermometer emersion correction. Daniels has given a stem correction for partially submerged thermometers which was as follows:

> Thermometers are usually calibrated for total immersion of the mercury and a correction is necessary when part of the stem is exposed. The thermometer will read too low if the air surrounding the stem is colder than the bath in which the bulb is immersed, and too high if the air is warmer. A second thermometer is placed near the exposed stem and the stem correction, S, is given by the formula
>
> $S=0.00016n(T-t)$
> where n-length of exposed mercury column in terms of scale degrees.
> T=temperature of "bath" (oven)
> t=average temperature of emergent stem.

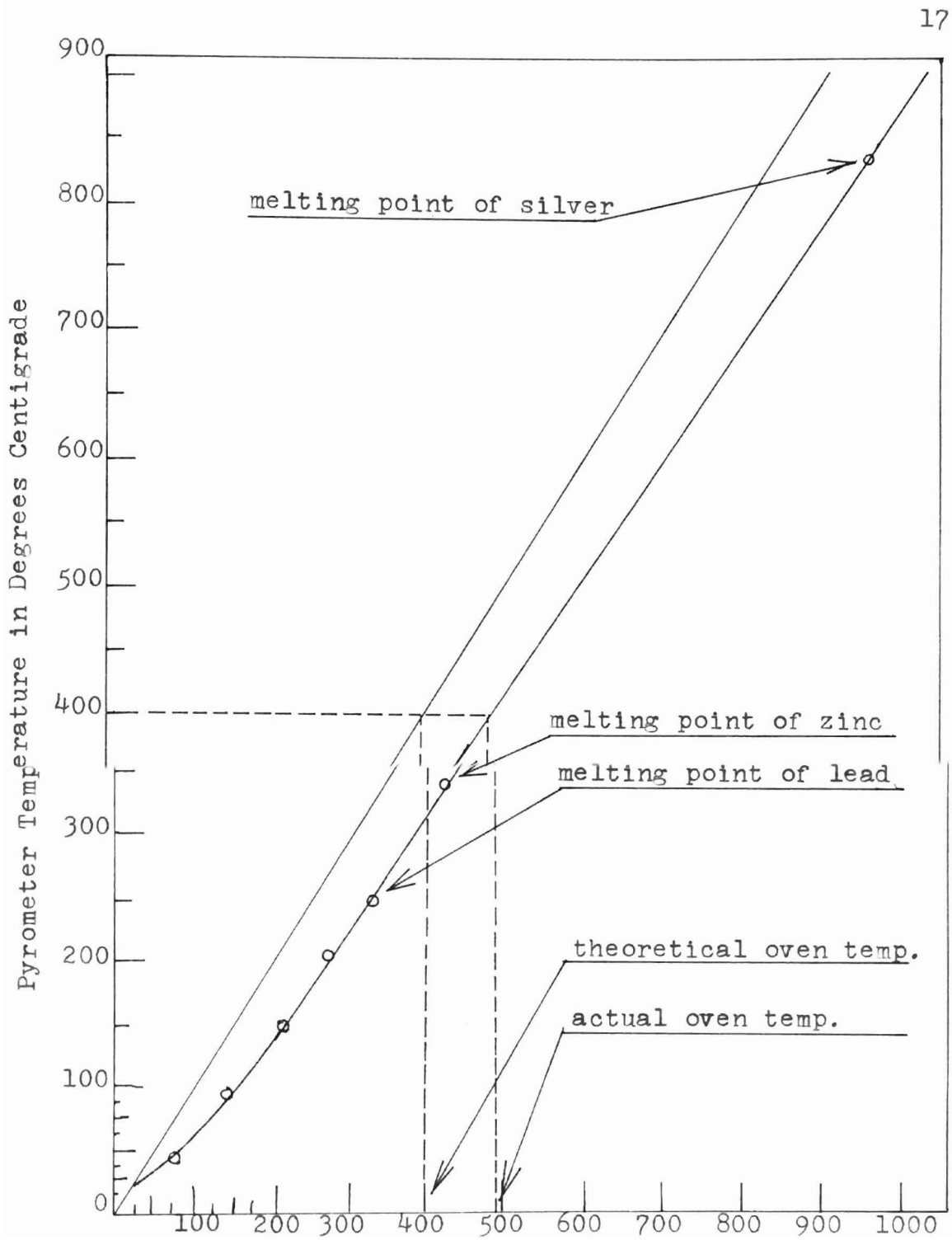

Figure 2. Pyrometer Reading versus Actual Oven Temperature.

The factor 0.00016 is suitable for the glass used in most thermometers.[1]

At a pyrometer setting of 204°C, the thermometer registered, on an average, 261°C as illustrated in Table I. The thermometer was "submerged" into the oven up to the 27°C Calibration.

Thus at 261°C;

$n=261^{\circ}C - 27^{\circ}C$ or $n=234^{\circ}C$

$T=261^{\circ}C$

$t=29^{\circ}C$ (determined with another thermometer)

therefore,

$S=(16 \times 10^{-5})\ (234)\ (232) = 8.7^{\circ}C$

Therefore, the actual temperature was the pyrometer reading plus "S" or 261°C plus 9°C or 270°C. Other values for three other temperatures were included in Table I.

Zero point of the balance as a function of temperature. The harness which held the crucible, as illustrated in Figure 1, was placed in the oven and was balanced with an equal weight at room temperature. The balance deviated by only three tenths of a milligram when the oven was heated up to 900°C. This change in weight was considered irrelevant to subsequent measurements.

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[1]Farrington Daniels, Experimental Physical Chemistry (New York: McGraw-Hill Company, 1941), p. 421.

TABLE I

STANDARDIZATION OF OVEN TEMPERATURE INCLUDING CORRECTION FOR INCREASED TEMPERATURE READING DUE TO PARTIAL THERMOMETER EMERSION

Pyrometer Reading	Temperature by Thermometer Individual Readings				Average	Additional Temperature "S"	Actual Temperature
* 38°C	69°C	72°C	74°C	76°C	73°C	0.3°C	73°C
* 93	145	139	137	139	140	2.0	142
* 149	219	209	215	214	211	5.3	216
* 204	251	269	260	261	261	8.7	270
+ 239	232	238	249	---	239	---	327
+ 328	329	321	335	---	328	---	419
+ 837	832	843	835	---	837	---	961

*Temperatures recorded by thermometer.

+Temperatures recorded by melting points of metals.

CHAPTER IV

THERMAL ANALYSIS

Introduction. The zinc borates examined in this study were known to contain water of hydration. The oven illustrated in Figure 1 was employed to determine the number of water molecules present. It was believed that any zinc borate molecules containing a definite ratio of water molecules should lose its water of hydration at specific temperatures. If two or more molecules of water were present, each water molecule per zinc borate "molecule" could, theoretically, be driven off at different temperatures. Therefore, a determination of the fractional weight loss of the three zinc borate samples was made.

Weight loss versus temperature. The samples were oven dried at 125°C for at least two days. Two gram samples were placed in oven dried crucibles and an analysis for weight loss was done immediately.

The samples were heated to predetermined temperatures which were selected from the pyrometer. The temperatures chosen for samples #112, 237, and 325 were shown in Tables II, III, and IV respectively.

The selected temperatures were held until the sample ceased to lose weight. When it was possible to zero the balance by removing weights, the weight loss was considered

TABLE II

AVERAGE PER CENT WEIGHT LOSS OF SAMPLE NO. 112
AT CONSTANT TEMPERATURES
(SAMPLES OVEN DRIED AT 125°C)

Pyrometer Temperature	Actual Temperature	Fractional Weight Losses For Three Analyses			Average Per cent Weight Loss
		No. 1	No. 2	No. 3	
50°C	90°C	0.	0.	0.	0
75	140	0.	.005	0.	.1
100	160	.005	.006	.007	.6
125	180	.042	.040	.040	4.1
150	210	.047	.049	.049	4.9
200	270	.066	.070	.069	6.8
250	320	.081	.082	.082	8.2
300	375	.087	.087	.087	8.7
400	490	.092	.090	.091	9.1
500	590	.092	.091	.092	9.2
600	705	.092	.091	.092	9.2
700	810	.092	.092	.092	9.2

TABLE III

AVERAGE PER CENT WEIGHT LOSS OF SAMPLE NO. 237
AT CONSTANT TEMPERATURES
(SAMPLES OVEN DRIED AT 125°C)

Pyrometer Temperature	Actual Temperature	Fractional Weight Losses For Three Analyses			Average Per Cent Weight Loss
		No. 1	No. 2	No. 3	
50°C	90°C	0.	0.	0.	0.
75	140	0.	0.	0.	0.
100	160	.027	.007	.014	1.6
125	180	.031	.032	.030	3.1
150	210	.071	.063	.062	6.5
200	270	.092	.090	.087	8.9
250	320	.106	.103	.102	10.4
300	375	.113	.110	.110	11.1
400	490	.118	.116	.114	11.6
500	590	.119	.117	.115	11.7
600	705	.119	.117	.115	11.7
700	810	.119	.117	.115	11.7

TABLE IV

AVERAGE PER CENT WEIGHT LOSS OF SAMPLE NO. 325
AT CONSTANT TEMPERATURES
(SAMPLES OVEN DRIED AT 125°C)

Pyrometer Temperature	Actual Temperature	Fractional Weight Losses For Three Analyses			Average Per Cent Weight Loss
		No. 1	No. 2	No. 3	
50°C	90°C	0.	0.	0.	0.
75	140	0.	.003	.001	.2
100	160	.002	.008	.005	.5
125	180	.017	.023	.025	2.2
150	210	.045	.043	.043	4.3
200	270	.062	.062	.062	6.2
250	320	.073	.070	.069	7.0
300	375	.078	.076	.075	7.6
400	490	.080	.079	.078	7.9
500	590	.081	.079	.078	7.9
600	705	.081	.079	.078	7.9
700	810	.081	.079	.078	7.9

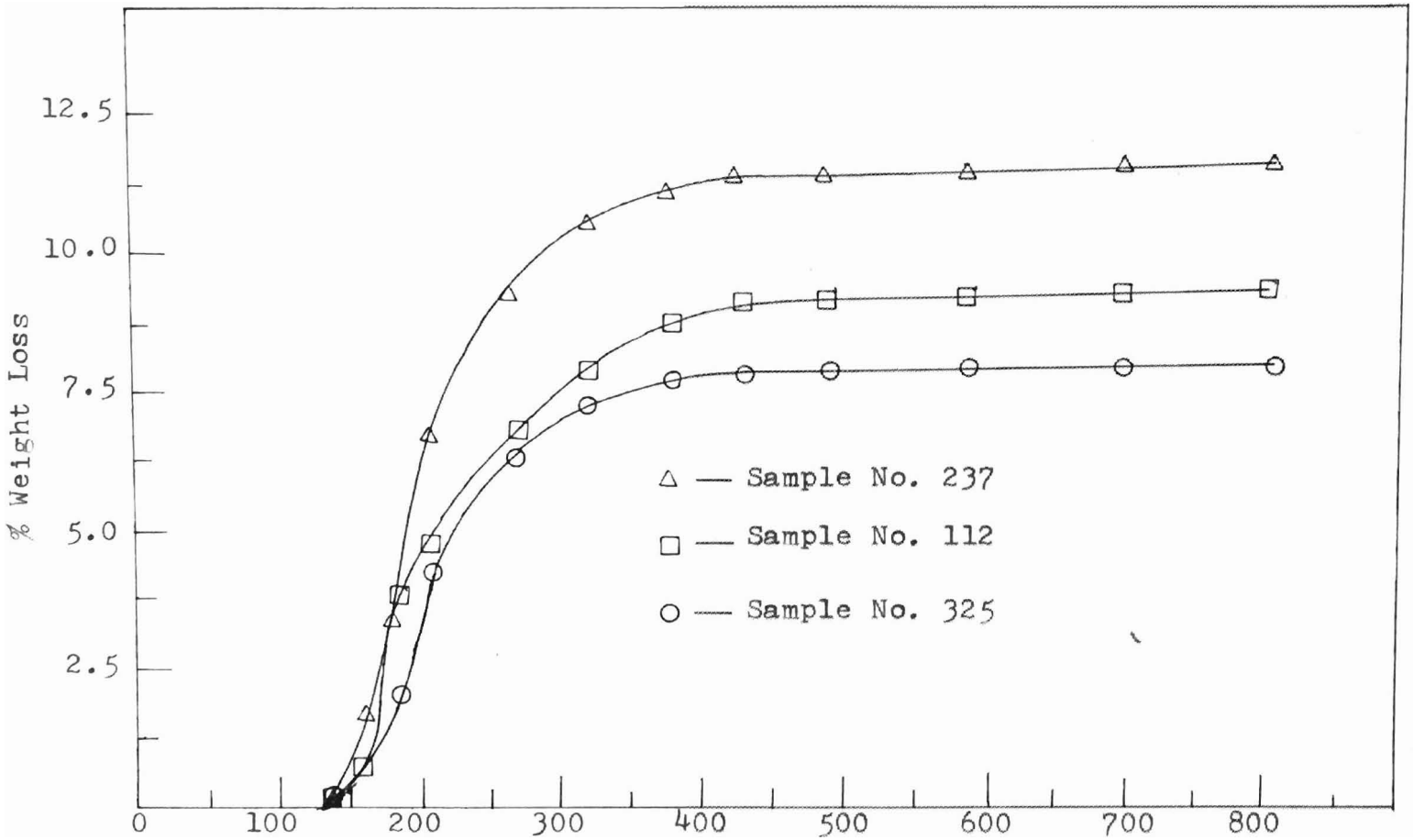

Figure 3. Per cent Weight Loss at Constant Temperatures For Oven Dried Samples.

complete at that temperature and the next higher temperature was selected.

After all weight-loss determinations were completed, a graph illustrating the per cent loss of each sample at specified temperatures was constructed (See Figure 2).

Commentary on Figure 3--Weight loss versus temperature. Approximately identical fractional weight losses for sample #112 and #237 were given off at temperatures up to 180°C. Sample #325 lost weight more slowly and was shown to contain the least amount of hydrated water per gram of oven dried sample.

The three zinc borates investigated in the study were prepared commercially by the Humphrey Chemical Corporation and an analysis for per cent composition and per cent loss of ignition has been published.

TABLE V

PER CENT COMPOSITION AND LOSS ON IGNITION OF ZINC BORATES

Designation	Zinc % as ZnO	Boron % as B_2O_3	% Loss On Ignition
ZB-112	45	35	20
ZB-237	33	41	26
ZB-325	52	29	19

*

*Humphrey Chemical Corporation, "ZB-112 · ZB-237 · ZB-325 (Zinc Borates)," Bulletin No. 201.

Humphrey stated in his bulletin that the borates were non-hygroscopic. Furthermore, ZB-237 was described as a borate containing a low per cent of zinc and having a low specific gravity. The ZB-325 was described as having a higher specific gravity and higher zinc content.

The weight loss versus temperature analysis as depicted in Figure 3 illustrated that the oven dried samples gave approximately one-half the total weight loss that was reported by Humphrey. Thus, the commercial laboratory has assumed that nearly all of the water which was driven off of the zinc borates was actually part of the zinc borate complex and was not absorbed water. Evidence for this was given from the smooth curve of the graph. If there was a transition from adsorbed water being driven off to hydrated water being driven off, the graph should have indicated this.

Relative total weight loss was in agreement with Humphrey's analysis, but the graph of Figure 3 cannot be considered to be an accurate quantitative analysis.

If two or more water molecules were associated with each borate "molecule", each molecule might have been driven off at different temperatures. This would have resulted in a step down weight loss transformation and the number of such steps would have been indicative of the number of water molecules associated with each borate. The graph clearly

indicated that no step down weight loss was achieved. The graph was smooth and all changes in slope were gradual.

A possible explanation for this was that only one water molecule was associated with each borate. However, each water molecule would have similar bonding and should have been driven off above a specific temperature.

However, the oven was held at a constant temperature until per cent weight loss ceased. Thus, hydrated molecules were being "boiled" off in gradual amounts rather than in discreet units.

Maximum weight loss was uniformly achieved for all three samples at 400°C. Figure 3 illustrated that no substantial weight loss occurred above this temperature. Other samples were subjected to temperatures slightly in excess of 1100°C and no further weight loss occurred.

Weight loss versus time. Undried zinc borates were analyzed by measuring fractional weight loss at constant time intervals as the oven was heated up in a uniform manner. Two gram samples were placed in the oven at room temperature and the oven's pyrometer was turned to the maximum reading. Thus, the oven's temperature increased at a maximum rate. A uniform heating rate was established by this method and the oven's temperature increased approximately 50°C every minute. While the oven's temperature was being increased per cent weight losses were recorded each

minute. It was felt that this was a more objective means of determining the possibility of a step-down weight loss than was the determination of temperature versus weight loss. It also served as a convenient cross check.

In the weight loss versus temperature determination (Figure 3) there existed the possibility that the "corners" of the expected steps, due to step-down weight loss, were plotted.

Commentary on Figure 4--Weight loss versus time. The results of the time versus weight loss study were illustrated in Figure 3 and data for samples #112, 237, and 325 were recorded in Tables VI, VII, and VIII respectively.

Figure 4 definitely illustrated that the water molecules were not driven off in a "step-down" weight loss transformation, but were "boiled" off as was formerly indicated in Figure 3.

A comparison of Figures 3 and 4 revealed a significant difference in total weight lost. The samples which were oven dried at 125°C were considered in Figure 3 and the samples which were not dried were considered in Figure 4. The non-dried sample had a weight loss of nearly twice that of the oven dried sample. The results for total weight loss was in fairly close agreement to the values listed in Humphrey's analysis as recorded in Table V. The relative humidity was very high (almost 100 per cent) while the non-

TABLE VI

AVERAGE PER CENT WEIGHT LOSS OF SAMPLE NO. 112 DURING EQUAL TIME INTERVALS AND CONSTANT RATE OF TEMPERATURE INCREASE (SAMPLES NOT OVEN DRIED)

Pyrometer Temperature	Actual Temperature	Time Elapsed (Minutes)	Fractional Weight Loss For Two Analyses		Average Per Cent Weight Loss
22°C	22°C	0	0.	0.	0.
22	22	1	0.	0.	0.
45	75	2	0.	0.	0.
75	140	3	.006	.005	.5
115	170	4	.038	.037	3.7
160	220	5	.083	.082	8.2
200	270	6	.130	.129	12.9
240	320	7	.172	.172	17.2
280	360	8	.205	.205	20.5
325	410	9	.228	.228	22.8
370	455	10	.240	.239	23.9
400	485	11	.245	.245	24.5
430	515	12	.246	.245	24.6
470	545	13	.246	.245	24.6
500	590	14	.246	.245	24.6

TABLE VII

AVERAGE PER CENT WEIGHT LOSS OF SAMPLE NO. 237 DURING EQUAL TIME INTERVALS AND CONSTANT RATE OF TEMPERATURE INCREASE (SAMPLES NOT OVEN DRIED)

Pyrometer Temperature	Actual Temperature	Time Elapsed (Minutes)	Fractional Weight Loss For Two Analyses		Average Per Cent Weight Loss
22°C	22°C	0	0.	0.	0.
22	22	1	0.	0.	0.
45	75	2	0.	0.	0.
75	140	3	.004	.004	.4
115	170	4	.031	.031	3.1
160	220	5	.079	.079	7.9
200	270	6	.127	.126	12.6
240	320	7	.175	.174	17.4
280	360	8	.215	.215	21.5
325	410	9	.246	.246	24.6
370	455	10	.270	.270	27.0
400	485	11	.281	.281	28.1
430	515	12	.288	.288	28.8
470	545	13	.290	.290	29.0
500	590	14	.290	.290	29.0

TABLE VIII

AVERAGE PER CENT WEIGHT LOSS OF SAMPLE NO. 325 DURING EQUAL TIME INTERVALS AND CONSTANT RATE OF TEMPERATURE INCREASE (SAMPLES NOT OVEN DRIED)

Pyrometer Temperature	Actual Temperature	Time Elapsed (Minutes)	Fractional Weight Loss For Two Analyses		Average Per Cent Weight Loss
22°C	22°C	0	0.	0.	0.
22	22	1	0.	0.	0.
45	75	2	0.	0.	0.
75	140	3	.003	.003	.3
115	170	4	.026	.026	2.6
160	220	5	.065	.066	6.5
200	270	6	.107	.107	10.7
240	320	7	.146	.146	14.6
280	360	8	.176	.176	17.6
325	410	9	.196	.197	19.6
370	455	10	.209	.209	20.9
400	485	11	.214	.215	21.4
430	515	12	.215	.215	21.5
470	545	13	.215	.215	21.5
500	590	14	.215	.215	21.5

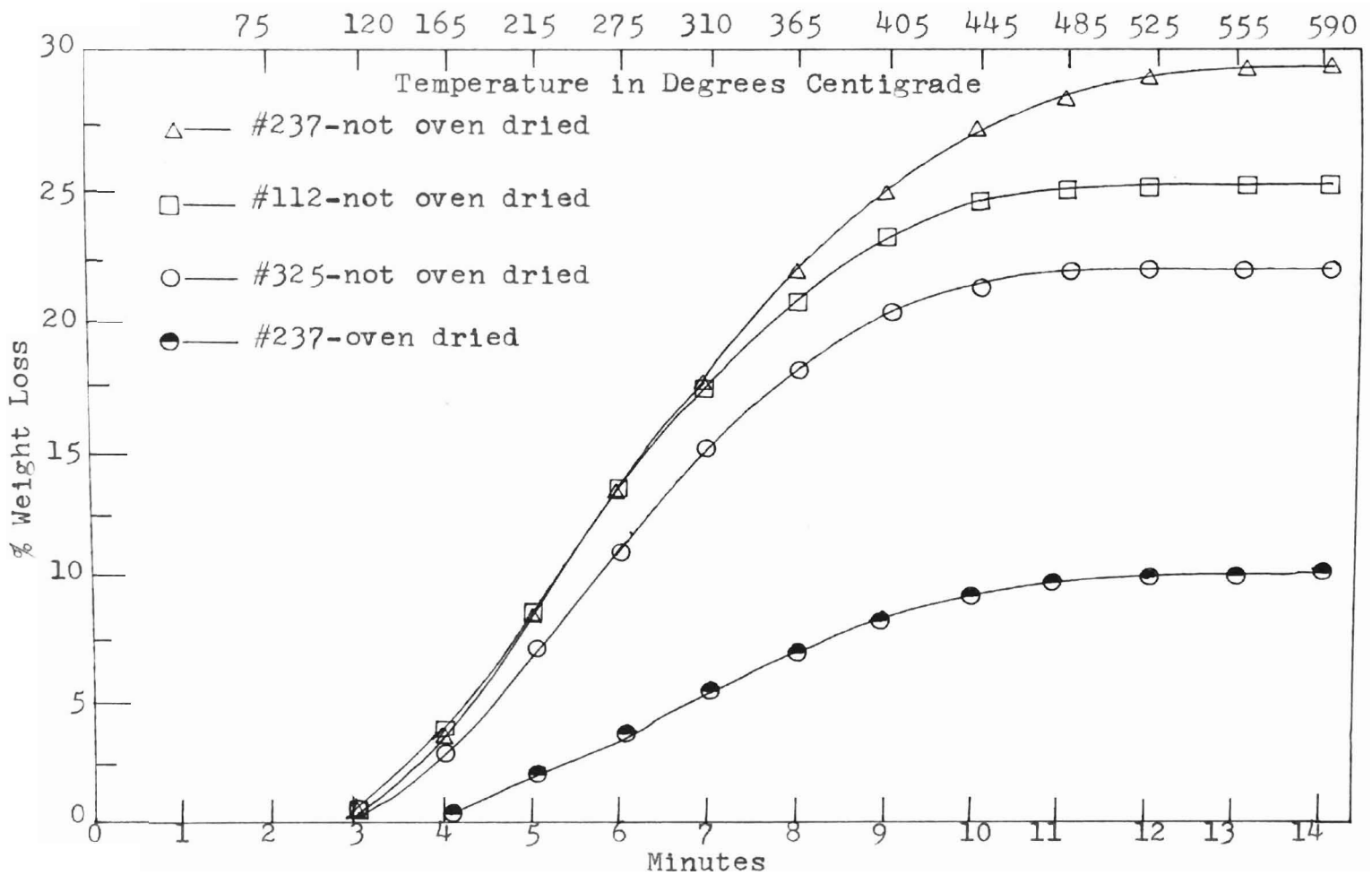

Figure 4. Per cent Weight Loss at Constant Time Intervals and Constant Rate of Temperature Increase For Non-Oven Dried Samples.

oven dried samples were studied for per cent weight loss.

Humphrey's analysis indicated an almost identical per cent weight loss on ignition for sample #112 and 325. The temperature versus time analysis indicated that the actual weight loss for sample #112 was about 24.5 per cent rather than 20 per cent as was indicated in Table V. Humphrey also indicated in Table V that sample #325 had only 1 per cent less water content than sample #112. The data obtained for these samples (Table VI and VII) indicated a difference of 3.1 per cent. However, the samples investigated in this study were received from the Humphrey laboratory approximately one year prior to the printing of Table number V.

Furthermore, Humphrey stated in his bulletin that the results indicated in Table V are not definite for each borate. This was further substantiated by the number of significant figures used in the table.

Figure 4 revealed that the rate of weight loss was uniform for the three borates. However, as indicated in Figure 3, sample #325 did have a slower rate loss of weight than did the other two borates. Sample #112 and 237 had almost identical rates of weight losses for the first seven minutes. After seven minutes the oven had attained a temperature of 310°C.

No weight loss was observed until 120°C. Thus, the samples were concluded to be very non-hygroscopic because

adsorbed water would have come off at a much lower temperature.

After the oven had attained a temperature of 500°C, the weight loss was complete for all samples. The time required for the oven to go from room temperature to 500°C was about 12 minutes.

Figure 4 illustrated the difference in rate of weight loss of water from an oven dried sample (#237) and a borate which was not oven dried. The non-oven dried sample had a per cent weight loss of nearly 2.5 times as great as did the sample dried at 125-130°C for several days. Thus, even though the samples did reach a maximum weight loss at chosen temperatures (See Figure 3), they would continue to lose weight on prolonged standing at a constant temperature. This weight loss was so gradual that it could not be detected with an analytical balance.

A study of weight loss on ignition was done on each borate and the results obtained were identical to the total per cent weight loss obtained from the weight loss versus time study and reported in Tables VI, VII, and VIII.

Thermocouple analysis. A melting point determination was originally attempted by visual means. A crucible containing a five gram sample of zinc borate was placed in the oven. A short range telescope was constructed and an

attempt was made to determine the melting point of the borate by visual means. The borates contracted to approximately one-fifth of their original volume as the temperature exceeded 600°C. A definite melting point was not established by visual means. The sample appeared to approach a fluid state very gradually.

A second attempt was made to determine the melting point by rate of change of temperature of the oven with respect to time. A ten gram sample was placed in the oven and the oven's temperature was increased at a maximum rate. A graph of rate of change of temperature versus time was constructed. On such a graph the melting point would have been indicated by a slight decrease in rate of increase of the oven's temperature. No decrease was indicated from the graph, probably because the oven's heat capacity greatly exceeded that of the sample's.

A third attempt to determine the borate's melting point was attempted using a thermocouple of alumel and chromel wire. A five gram sample was placed in the oven as illustrated in Figure 1. The chromel-alumel thermocouple was placed in the sample and the oven's temperature was increased at a uniform rate. This proved to be unsuccessful because the amplitude of the strip chart recorder had to be decreased drastically to record the voltage produced by the large temperature increase. The thermocouple had to be

placed in the powdery zinc borate sample below 600°C. Above 600°C the borate sample contracted and became very hard.

Differential thermal analysis. A melting point determination was achieved for each borate by using differential thermal analysis. A double thermocouple of alumel and chromel was employed as indicated in Figure 1. Five grams of the powdery borate samples were placed in a crucible at room temperature. A strip chart recorder plotted any change in potential of the double thermocouple as the oven's temperature was increased to beyond the sample's melting point. The results for the three zinc borates were recorded in Figure 5.

A deflection towards the bottom of the graph indicated an endothermic reaction in which the temperature inside the crucible was less than the temperature outside. An exothermic transformation inside the crucible made the sample's temperature greater than the sample's environmental temperature and the strip chart recorder was deflected towards the top of the graph.

The differential thermal analysis was not a quantitative analysis in that no numerical heat units were assigned to the deflection produced by the change in potential of the double thermocouple. However, relative heat transformations were very indicative of the samples.

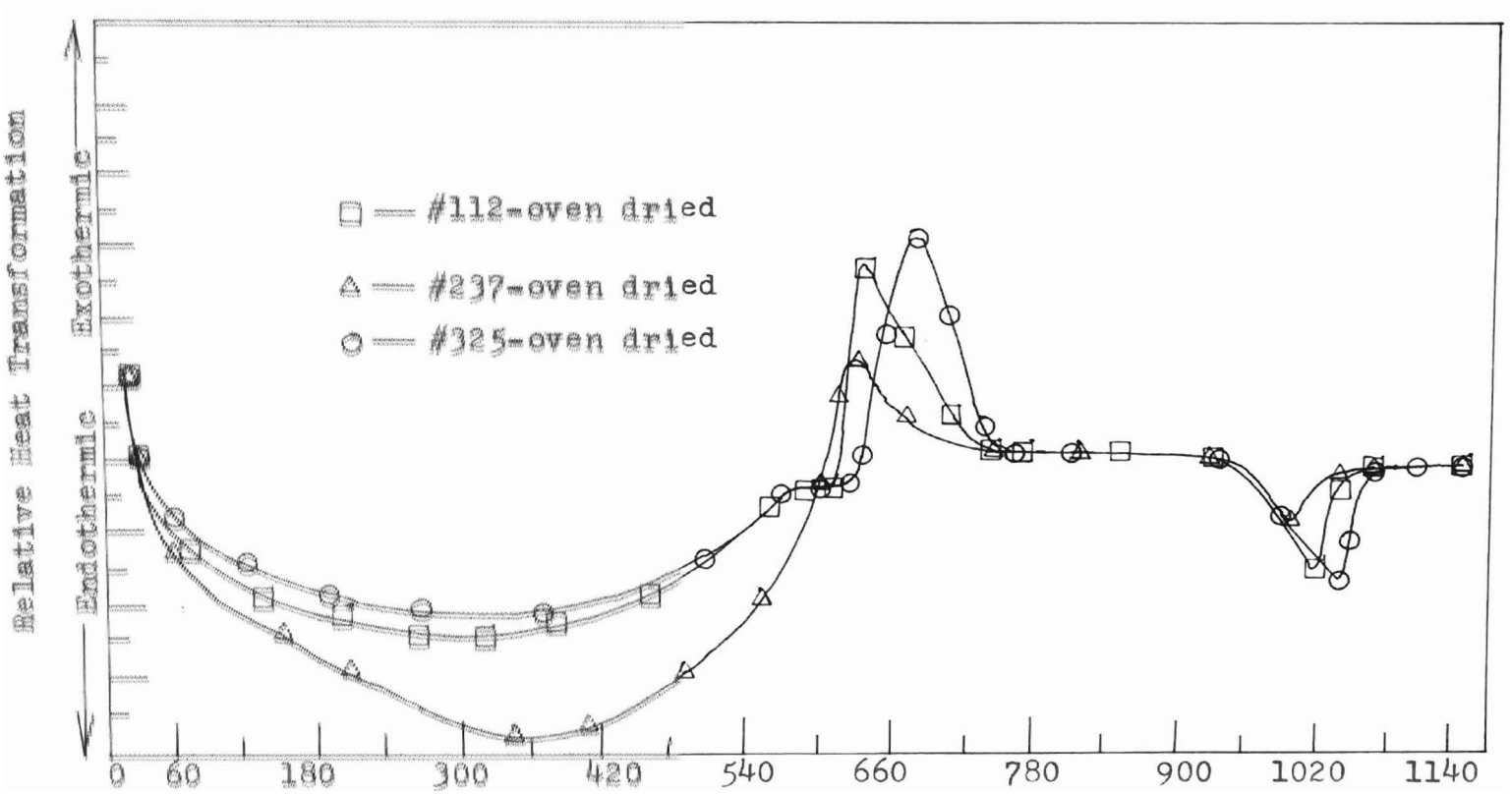

Figure 5. Differential Thermal Analysis of Three Zinc Borates.

Commentary on Figure 5--Differential thermal analysis. All samples were oven dried at 125°C and the thermal analysis was begun at room temperature.

Figure 5 indicated that an endothermic transition took place immediately following 24°C or room temperature. The smooth curve beginning at room temperature and continuing to approximately 600°C was due to the emanation of water from the zinc borates. Ideally, the endothermic curve should have begun at 125°C, the temperature at which the samples were dried. However, probably at lower temperatures the samples had a substantial lag relative to the environmental temperature of the oven chamber. This effect would have become nominal at high temperatures.

Since the dehydration curves were smooth, it was again established that the water of hydration was not driven off in discreet units corresponding to the number of water molecules associated with each borate. The water molecules were shown to be driven off uniformly. Similar results were illustrated in Figures 3 and 4.

The relative magnitudes of the endothermic dehydration curves were in complete agreement with previous data as illustrated in Figures 3 and 4. Sample #325 had an endothermic deflection slightly less than sample #112. This was in excellent agreement with Humphrey's analysis as recorded in Table V. Sample #237 was shown to contain a larger endo-

thermic deflection than the other two borates. This also corresponded to Table V and Figures 3 and 4.

The relative magnitudes of the exothermic peaks near 600°C and near 1000°C were inversely related to the amplitude of the dehydration curves. Thus, the samples contain- the greatest per cent of water had a smaller per cent of zinc and boron which was substantiated by the amplitudes of the peaks at 600°C and 1000°C.

Sharp peaks were indicated for exothermic transitions nears 600°C and for endothermic transitions near 1000°C. Thus, the heat transformations were regarded as a qualitative means of identifying any sample.

It was shown from Figure 5 that the graphs of all three samples did not return to the "neutral" position between the endothermic and exothermic heat transformation. However, all samples consistently returned to the same ordinate position, which was an indication of the reproducibility of the data. The reproducibility was checked for each sample. The graphs were almost identical and any descrepancy between the graphs of the same sample could not be recorded on a graph having the dimensions of Figure 5.

Harrison and Hummel[1] have studied phase equilibria for zinc oxide-boron oxide systems and have found that low

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[1]D. E. Harrison and F. A. Hummel, "Phase Equilibria and Fluorescence in the System Zinc Oxide-Boric Oxide," Journal of the Electrochemical Society, CIII (September, 1956), 491.

temperature (α) $ZnO \cdot B_2O_3$ inverted sluggishly to the cubic high temperature (β) $ZnO \cdot B_2O_3$ at 600°C and determined the melting point of this borate to be 982°C ± 3°C.

Ingerson, Morey, and Tuttle investigated the $ZnO \cdot B_2O_3$ system and the results were recorded in Table IX.

TABLE IX

LIQUIDUS DETERMINATIONS IN THE SYSTEM $ZnO-B_2O_3$

Designation	Composition Weight % ZnO	Composition Weight % B_2O_3	Liquidus Temperature °C	Primary Phase
1	47.2	52.8	998	2 liquid layers
2	53.6	46.4	998	$ZnO \cdot B_2O_3$
3	59.3	40.7	1001	$ZnO \cdot B_2O_3$
4	63.9	36.1	998	$ZnO \cdot B_2O_3$

*

*Earl Ingerson et al., "The Systems $K_2O-ZnO-SiO_2$, $ZnO-B_2O_3-SiO_2$," American Journal of Science, XXXI (April, 1948), 37.

CHAPTER V

PER CENT COMPOSITION ANALYSIS

Refractive index analysis of zinc borate glasses. Harrison and Hummel[1] in 1956 analyzed several zinc borates for ZnO and B_2O_3 compositions. They prepared varying proportions of ZnO and H_3BO_3 by mixing the correct ratios in an agate mortor with reagent grade acetone until it evaporated and a white powder resulted.

It was stated that calcines were prepared in platinum crucibles at temperatures ranging from 500°C to 980°C with firing times ranging from 10 hours to 6 weeks.

Although it was not clear from Harrison and Hummel's article, it appeared that the glasses were made from the calcines. Calcines referred to dried zinc borates. They felt that the investigation of the system might be complicated by compositional changes during the original melting of the glasses or later during the quench work. To assess this possibility, the 1:1 composition which had been prepared as a calcine and by fusion was analyzed by chemical and ignition loss methods. Harrison and Hummel also stated that at greater than 70.0 per cent ZnO, it was impossible to retain a glass no matter how rapidly the sample was quenched.

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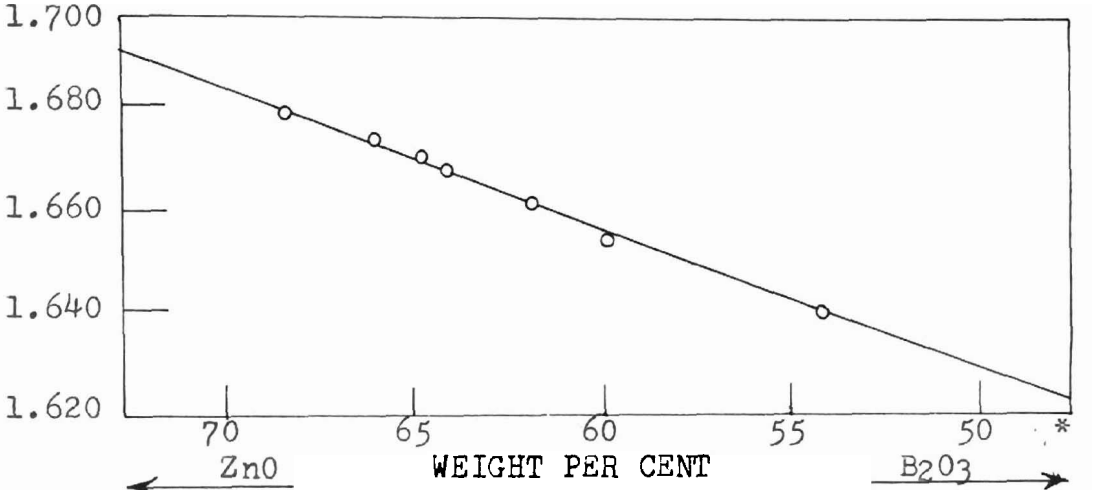
[1]Harrison and Hummel, op. cit., p. 496.

The graph of refractive index of varying compositions of zinc borate glasses were indicated by Harrison and Hummel and is shown below.

FIGURE 6

REFRACTIVE INDEX VS. COMPOSITION FOR ZINC OXIDE-BORIC OXIDE GLASSES



Harrison stated that the immersion technique was used to determine the refractive indexes of glasses and crystals to an accuracy of ±0.002, using white light and index oils which were calibrated with an Abbe refractometer. Measurements of refractive indexes in this study also employed an Abbe refractometer and an index oil. A standardized cube of glass was used to standardize the instrument.

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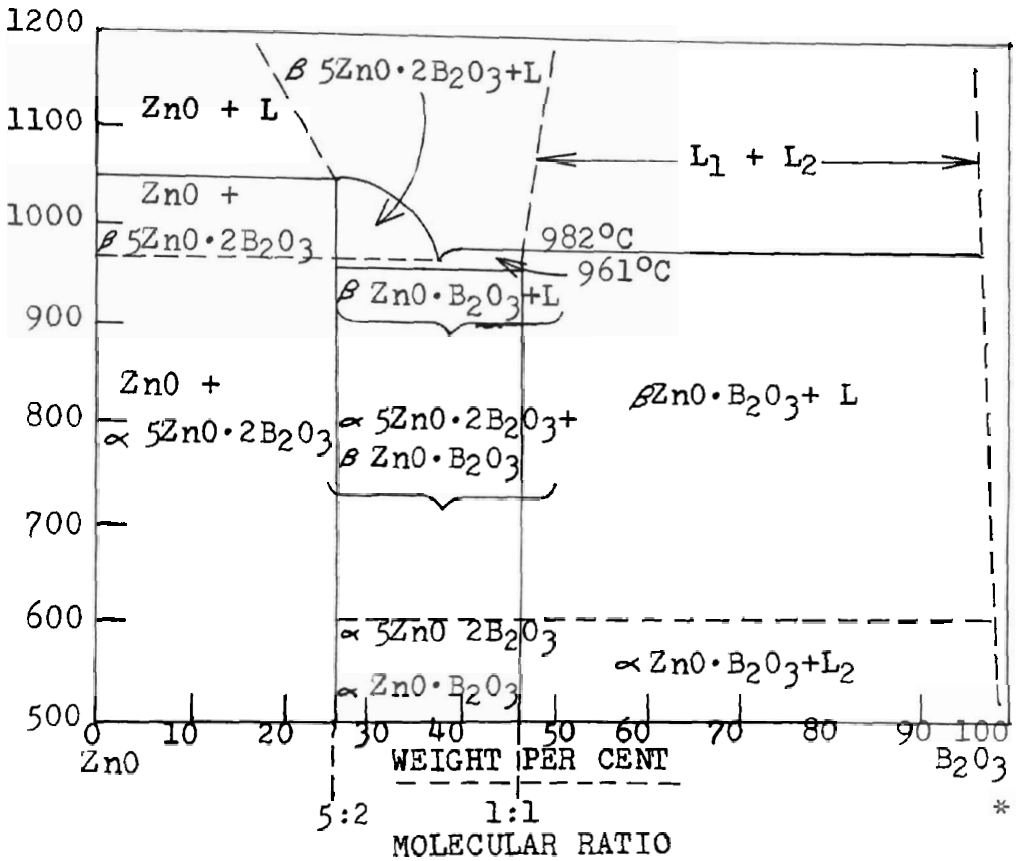
*Ibid.

Harrison and Hummel also made an examination of the borates for polymorphic inversion at high temperatures.

FIGURE 7

THE SYSTEM $ZnO \cdot B_2O_3$



Harrison also stated that the original starting material contained no high temperature $ZnO \cdot B_2O_3$. The beta form was described as having a cubic structure.

Harrison and Hummel determined a rate of inversion of α to β $ZnO \cdot B_2O_3$ at various high temperatures.

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*Ibid.

At 713°C approximately 70 per cent of the alpha form had inverted to the beta form after 75 hours of firing time. At 740°C approximately 30 per cent had inverted to the beta form after 13 hours of firing time. At 786°C approximately 60 per cent of the $ZnO \cdot B_2O_3$ had inverted to the beta form after 13 hours. Thus, the glass samples of Harrison and Hummel were converted primarily to the beta form if they were prepared from the calcines. It was very evident from their graph that at higher temperatures, the rate of inversion from the alpha to the beta form increased very rapidly. However, no rates were indicated for samples heated to the borate's melting point of about 1000°C. It was observed from their graph of rate of beta inversion that at temperatures close to the melting point of the borates that a very high percentage of the borates were immediately converted to the beta form.

Preparation of glass samples for refractive index analysis. The glasses were prepared from 5 grams of the powdery borates which were weighed into porcelain crucibles. The samples were placed in an oven at a temperature slightly above the borate's melting point of approximately 1000°C and allowed to remain at a temperature above the melting point for ten minutes. The samples were quenched quickly by subjecting them to room temperature until cool. Clear glasses resulted from every borate, however, often the borates would

crack upon cooling and were discarded.

The glasses were cut with a circular diamond edged saw. Special precaution was taken by polishing the glasses with a glass grinding wheel which was sprayed with water. The water served as an aid to obtaining a smoother surface and also kept the glasses at a lower temperature while being ground. Further polishing, if necessary, was done with an abrasive of aluminum oxide on a sheet of plate glass. Special caution was taken to make the zinc borate glasses have two flat adjacent sides with a right angle between these sides.

An Abbe refractometer was used for refractive index measurements. The glasses were held in place on the refractometer by an index liquid of alpha-Bromonaphthaline.

A table of the results obtained for the 3 zinc borates and for a special zinc borate which was artifically made for reference were listed in Table X.

Each refractive index listed in Table X was done on a different sample. Identical refractive indexes were obtained for sample #112 and 237. Sample #325 gave refractive indexes slightly higher than the other two samples. Assuming a refractive index for sample #325 as indicated in Table IX, Figure 6 gave a value for the per cent composition of ZnO to be about 57 per cent.

TABLE X

REFRACTIVE INDEXES OF ZINC BORATE GLASSES

Designation	Refractive Index of Sample No: 1	2	3	4
ZB-112	1.6345	1.6342	1.6342	---
ZB-237	1.6345	1.6345	1.6348	---
ZB-325	1.6485	1.6485	1.6475	---
57% ZnO Preparation	1.6334	1.6346	1.6345	1.6346

An artificial sample of ZnO and H_3BO_3 was mixed to give a borate containing 57 per cent ZnO. This mixture was melted at about 1050°C for ten minutes and quenched in air.

The commercial laboratory from which the borates were obtained indicated that the per cent of ZnO in samples #112, 237, and 325 were different (See Table V). Therefore, the refractive index of each sample should have been different. Thus, it was concluded that the refractive index method was not a valid means of determining the per cent composition of ZnO and B_2O_3 in the borates.

Classical chemical analysis of zinc borates. Snell and Bikfen[1] outlined a classical volumetric analysis for

[1]Foster D. Snell and Frank M. Bikfen, Commercial Methods of Analysis (New York: Chemical Publishing Company, 1964), pp. 504-506.

ZnO. The zinc was precipitated by potassium ferro-cyanide as white $K_2Zn_3[Fe(CN)_6]_2$. Two drops of a very dilute solution of $FeCl_3$ was used to render the solution bluish until the end point was approached.

A dilute solution of uranyl acetate, slightly acidified with acetic acid, was used as an external indicator on a spot plate. The end point was determined by a brown tinge appearing in the indicator approximately 30 seconds after a drop of the zinc solution was added. The results obtained were recorded in Table XI.

TABLE XI

MILLILITERS OF $K_4Fe(CN)_6$ REQUIRED FOR PRECIPITATION OF Zn

Sample No.	Mls. For Precipitation			Average Mls.
ZB-112	13.37	13.01	13.28	13.21
ZB-237	10.42	10.73	10.50	10.55
ZB-325	15.36	15.39	15.26	15.34

Loss on drying for the three samples at 90°C for two hours was recorded in Table XII.

TABLE XII

PER CENT WEIGHT LOSS FOR SAMPLES DRIED AT 90°C

Sample No.	Fractional Weight Loss		Avg. % Loss
ZB-112	.0054	.0051	.52
ZB-237	.0052	.0055	.53
ZB-325	.0051	.0053	.52

The zinc borates were considered to be non-hygroscopic and no corrections were made for the per cent compositions recorded in Table XIII which were done on non-oven dried samples. Standardization of the $K_4Fe(CN)_6$ solution revealed 1 milliliter of the solution to be equivalent to .0063 grams of ZnO.

TABLE XIII

PER CENT WEIGHT COMPOSITION OF ZINC BORATE SAMPLES #112, 237, AND 325

Sample No.	%ZnO	% Loss On Ignition	% B_2O_3 by Difference
ZB-112	41.5	25.2	33.3
ZB-237	33.4	29.1	37.5
ZB-325	48.2	22.0	29.8

Loss on ignition for the non-oven dried samples was recorded in Table XIII. The samples were heated to 800°C for one hour.

The per cent of B_2O_3 in the three zinc borates was obtained by subtracting the per cent of ZnO and the per cent of H_2O for each sample from a theoretical 100 per cent for these three constituents. The results were recorded in Table XIII.

Mole ratio of $ZnO:B_2O_3$ from per cent composition analyses. Theoretical mole ratios of ZnO to B_2O_3 were

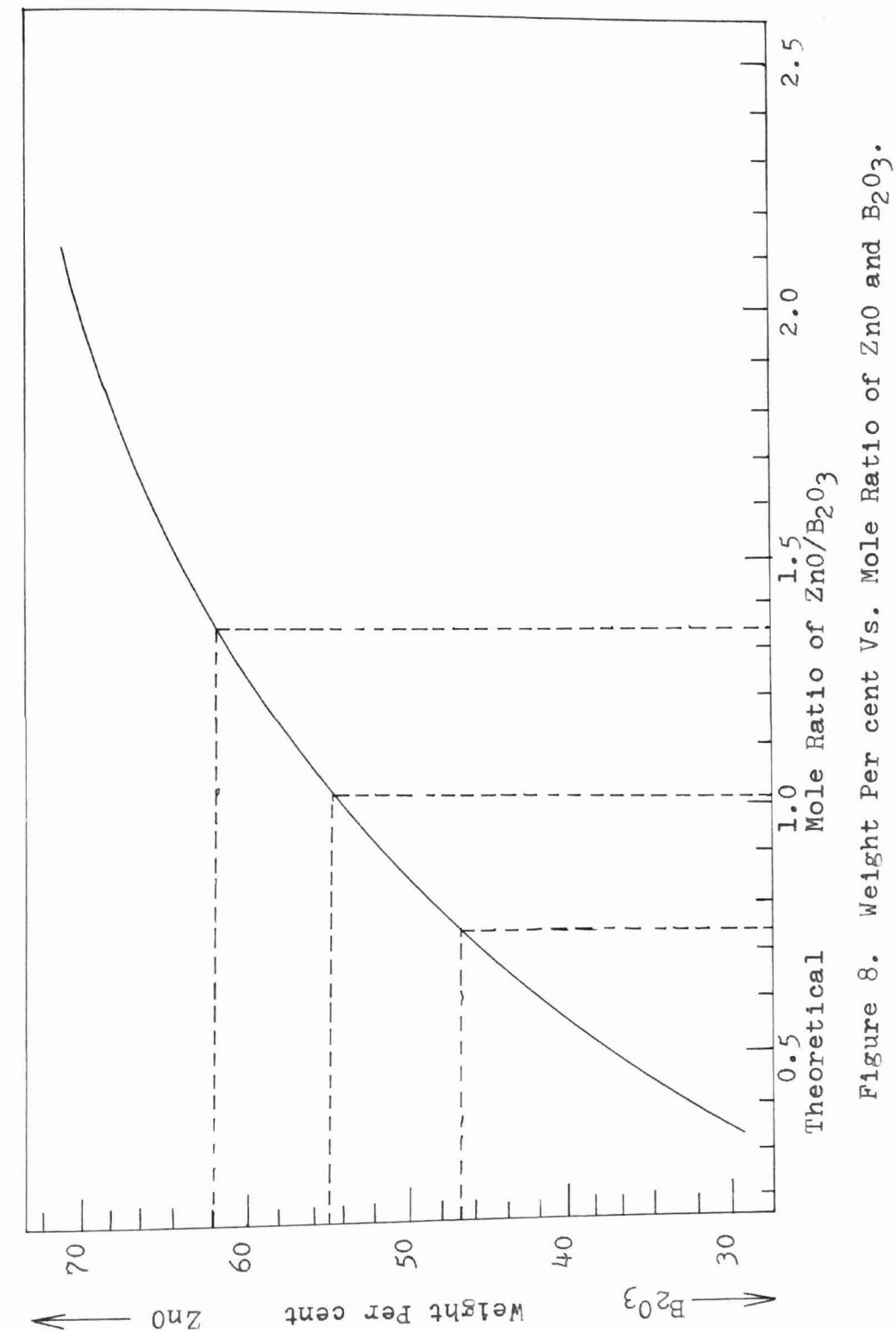

Figure 8. Weight Per cent Vs. Mole Ratio of ZnO and B_2O_3.

plotted against weight per cent of ZnO in a sample and were plotted in Figure 8. Molecular ratios of sample #112, 237, and 325 were "read" from the figure, assuming that the borates were totally composed of ZnO and B_2O_3 after the water of hydration had been removed. The values for the per cent composition of ZnO and B_2O_3 were obtained by increasing their percentages by a factor which was directly proportional to the per cent of loss on ignition due to dehydration.

Figure 8 illustrated that sample #112, 237, and 325 had molecular ratios of $ZnO:B_2O_3$ of very nearly 1:1, 3:4, and 4:3 respectively.

Number of water molecules associated with each borate. Table XIII was constructed to illustrate the per cent ignition loss due to dehydration for various theoretical zinc borates.

Harrison and Hummel[1] did a per cent weight loss on ignition analysis for a 1:1 composition of ZnO and B_2O_3 and obtained a per cent loss on ignition of 27.5 per cent.

Boric acid, H_3BO_3, can be represented as having the following composition.

$$2H_3BO_3 \longrightarrow 3H_2O + B_2O_3$$

From Table XIV, a relationship between the number of H_2O molecules and ZnO and B_2O_3 was observed. Sample #112,

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[1]Harrison and Hummel, op. cit., p. 495.

TABLE XIV

THEORETICAL % LOSS ON IGNITION FOR THE SYSTEM $ZnO:B_2O_3$ FOR A VARYING NUMBER OF H_2O MOLECULES

Possible Ratios Of $ZnO:B_2O_3$	Theoretical Per Cent ignition Loss For Zinc Borates Due To A Specific Number Of Water Molecules											
	$1H_2O$	$2H_2O$	$3H_2O$	$4H_2O$	$5H_2O$	$6H_2O$	$7H_2O$	$8H_2O$	$9H_2O$	$10H_2O$	$11H_2O$	$12H_2O$
1:1	10.7	19.2	26.5	32.3								
1:2	7.6	14.0	19.7	24.6	28.9							
1:3	5.8	11.0	15.7	19.9	23.6	27.1						
2:1	7.2	13.4	18.9	23.6	27.7	31.6	35.0					
2:3	4.6	8.8	12.7	16.2	19.5	22.6	25.4	27.9				
3:2	4.5	8.6	12.3	15.8	19.0	22.0	24.9	27.2	29.6			
3:4	3.3	6.5	9.5	12.1	14.3	16.7	19.4	21.6	23.6	25.6	27.4	29.2
4:1	4.3	8.3	12.0	15.4	18.5	21.5	24.2	26.8	29.0	31.3	33.3	35.3
4:3	3.3	6.3	9.1	11.9	14.4	16.8	19.1	21.2	23.2	25.2	27.0	28.7
5:2	3.2	6.2	9.0	11.6	14.1	16.5	18.7	20.8	22.8	24.8	26.6	28.3

which had a composition very close to $1ZnO:1B_2O_3$, lost an equivalent of 3 H_2O molecules. Sample #237 and 325 had $ZnO:B_2O_3$ ratios of very nearly 3:4 and 4:3 respectively. These ratios lost approximately an equivalent of 12 and 9 H_2O molecules on dehydration respectively.

Thus, it appeared that a definite number of water molecules was associated with each borate and the number of such water molecules was directly proportional to the number of B_2O_3 ions in the whole borate molecule. Three molecules of water appeared to be associated with each borate ion.

Harrison and Hummel's value of a 27.5 per cent weight loss for a 1:1 $ZnO:B_2O_3$ composition was in close agreement with the direct proportion theory as determined in this study (See Table XIV).

CHAPTER VI

INFRARED SPECTRA ANALYSIS

Introduction. The study of organic compounds and the determination of their structure with the use of infrared spectra has been established for a considerable period of time. Inorganic compounds have also been studied in the liquid and gaseous state. In 1952, the potassium bromide pressed disc technique was introduced and it became possible to analyze many types of inorganic solids. It has only been in the last 15 years that borates have been studied by the pressed disc method.

Sample and instrument preparation. The zinc borates were prepared in a solid mixture containing 400 milligrams of KBr and .4 milligrams of a zinc borate. This corresponds to a .1 per cent mixture of zinc borate in KBr. All mixtures were compressed under a pressure of 20,000 pounds per square inch for 4 to 5 minutes.

Previous study of borates using the pressed disc method indicated that a .5 per cent mixture would be a suitable concentration. The .5 per cent mixture proved to be too concentrated.

All infrared spectra analyses, including the sample preparation, were conducted in the State Agricultural Laboratory in Des Moines, Iowa. A Beckman IR-4 Infrared

Spectrophotometer was employed. Single beam analysis was used on all reported spectra. Occasionally double beam analysis was employed with no appreciable change in spectral absorption frequencies.

The Beckman IR-4 was equipped with NaCl prisms and used a double monochromator to help cut down on stray radiant energy. All borates were analyzed with a manual slit width of 3 times the normal slit width which was programed into the Beckman instrument.

Infrared analysis. The IR-4 was purged from 1 to 16 microns to determine any absorptions either inherent in the optics of the instrument or due to the absorption of air. The results for the purging were recorded in Figure 9 and were indicated by the black curve.

A blank pellet containing 400 milligrams of pure KBr was analyzed for the above infrared range to determine any absorptions that could be attributed solely to the KBr molecule. The results were plotted in Figure 9 and were indicated by a dashed curve. All subsequent graphs of infrared spectra contained the blank KBr analysis for absorption references and to identify absorption peaks arising solely from the zinc borates.

The differential thermal data, illustrated in Figure 5, indicated critical temperatures at which the zinc borates should be studied. The borate samples which had been sub-

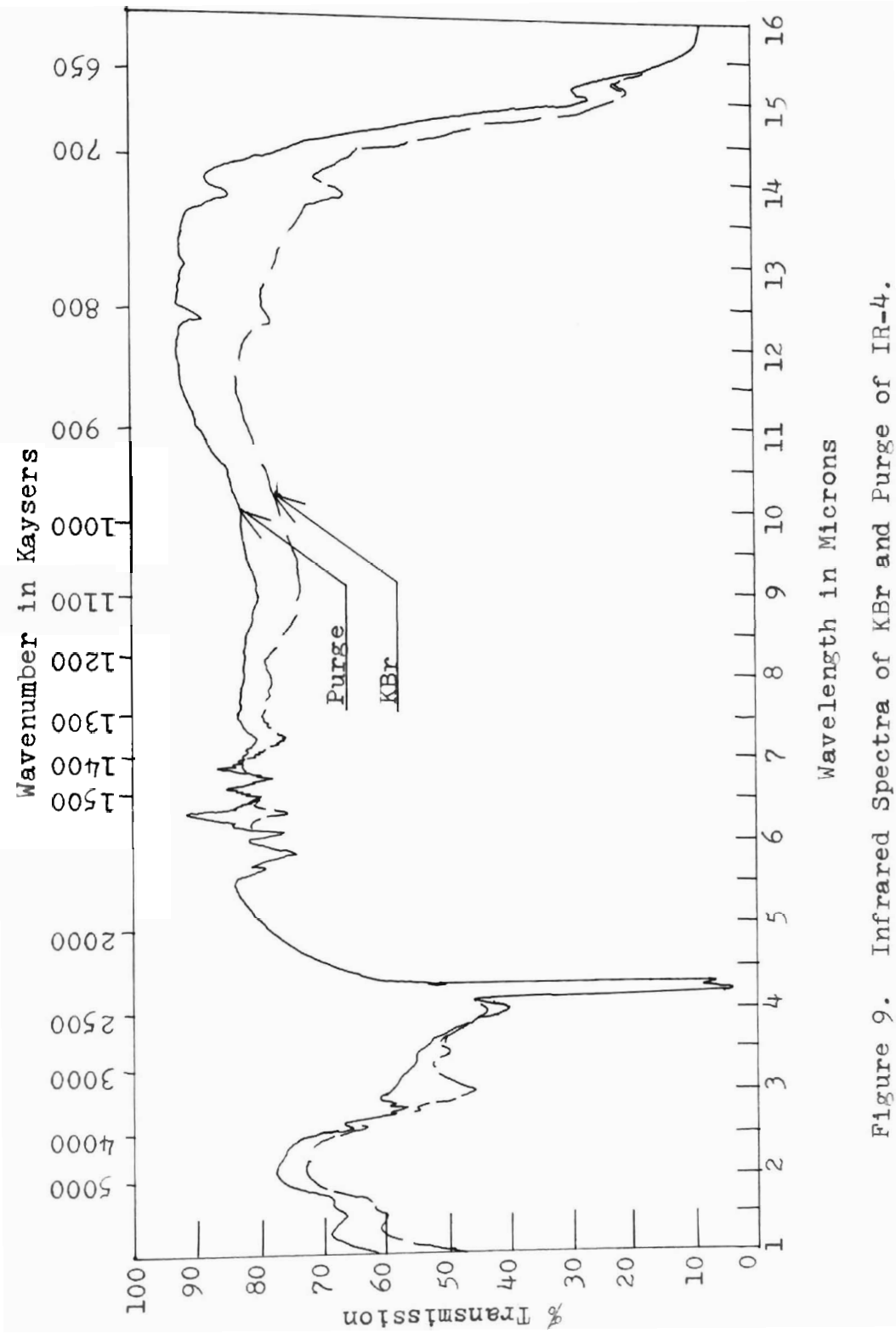

Figure 9. Infrared Spectra of KBr and Purge of IR-4.

jected to temperatures of 110°C, 590°C, 800°C, and 1080°C were investigated by infrared means at room temperature. The spectra of the three borates investigated in the study for the above temperatures were illustrated in Figures 10, 11, 12, and 13.

A comparison of Figures 10 and 11 indicated the difference between the spectra obtained for samples oven dried at 125°C and samples whichwere completely dehydrated at 585°C. Most of the absorption peaks at wavelengths longer than 8.5 microns were due primarily to water of hydration.

However, all samples when heated to a temperature of 800°C, which corresponded to the plateau in Figure 4, exhibited new absorption frequencies. At this temperature, as indicated in Figure 7, the alpha form of the borates had been converted to the beta form. Therefore, the new absorption peaks at the 800°C differential thermal analysis plateau were assigned to the beta form of the borates.

From the per cent composition analysis it was concluded that samples #112, 237, and 325 had molecular ratios of ZnO/B_2O_3 of approximately 1:1, 3:4, and 4:3 respectively. Harrison and Hummel found (See Figure 7) that the alpha form of the borates converted somewhat sluggishly to the high temperature cubic beta form. This conversion corresponded to the exothermic peak reported in the differential thermal analysis data in Figure 5. Harrison and Hummel's graph

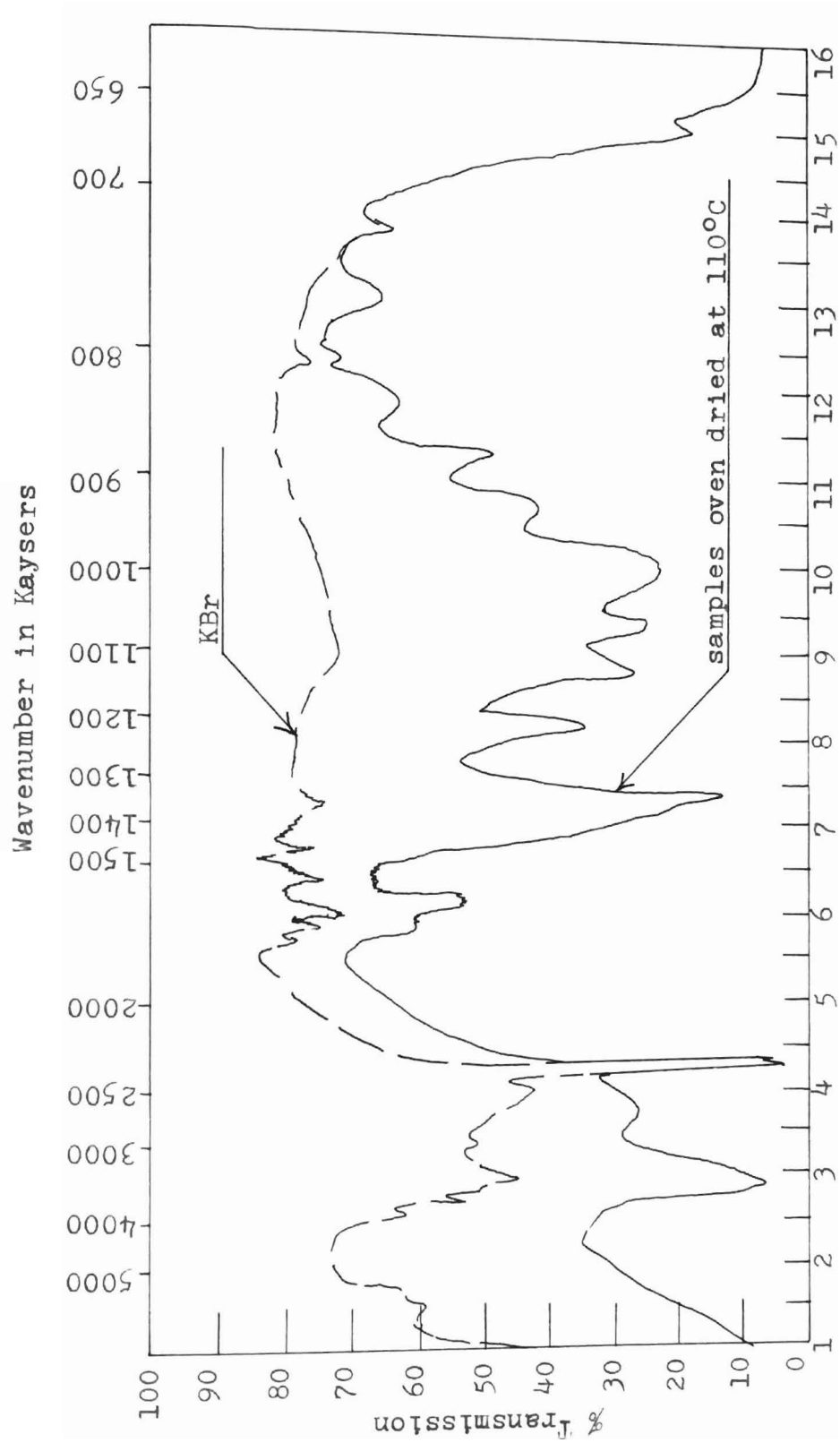

Figure 10. Infrared Spectra of Zinc Borates Heated at 110°C and Blank KBr.

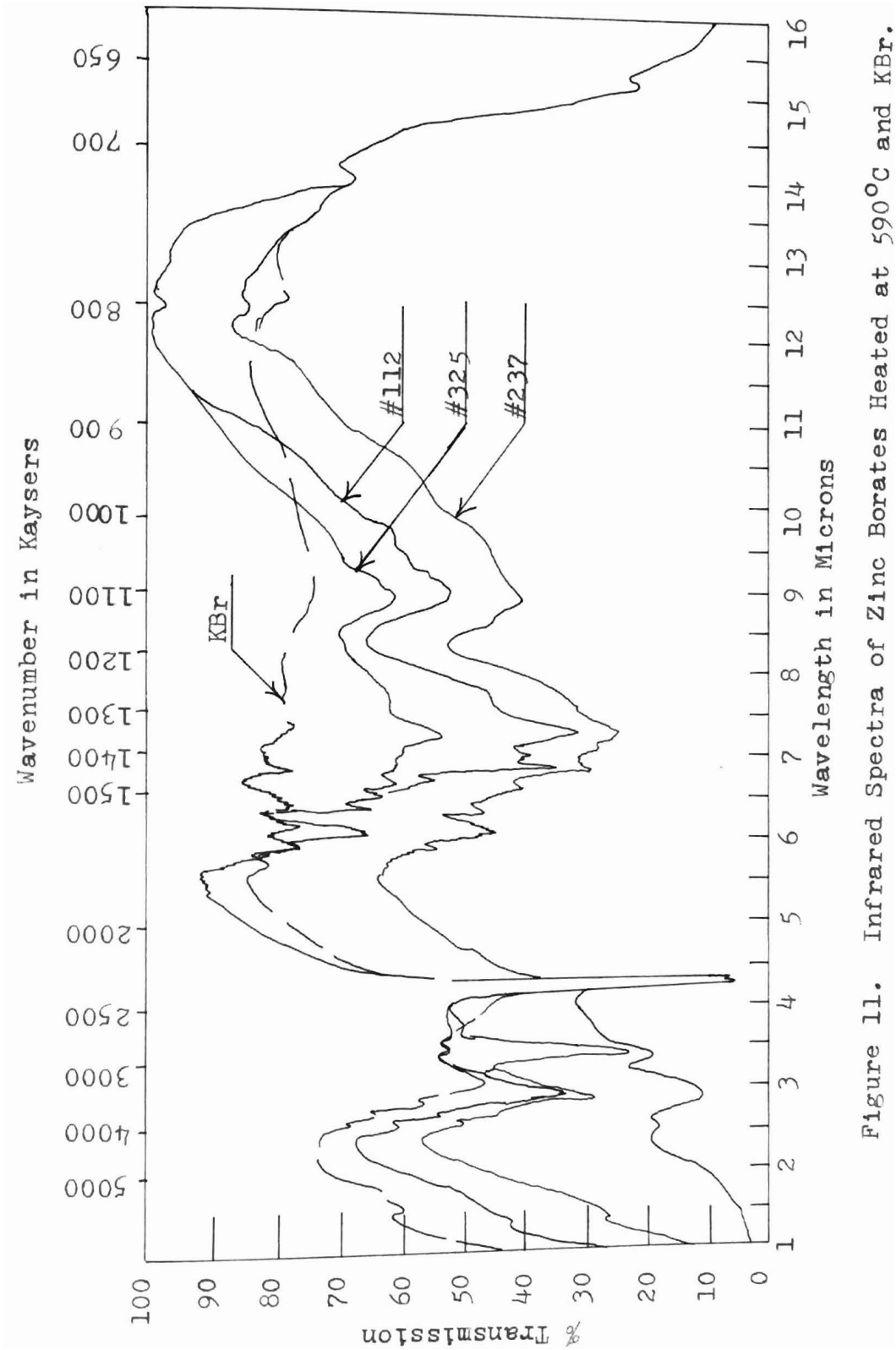

Figure 11. Infrared Spectra of Zinc Borates Heated at 590°C and KBr.

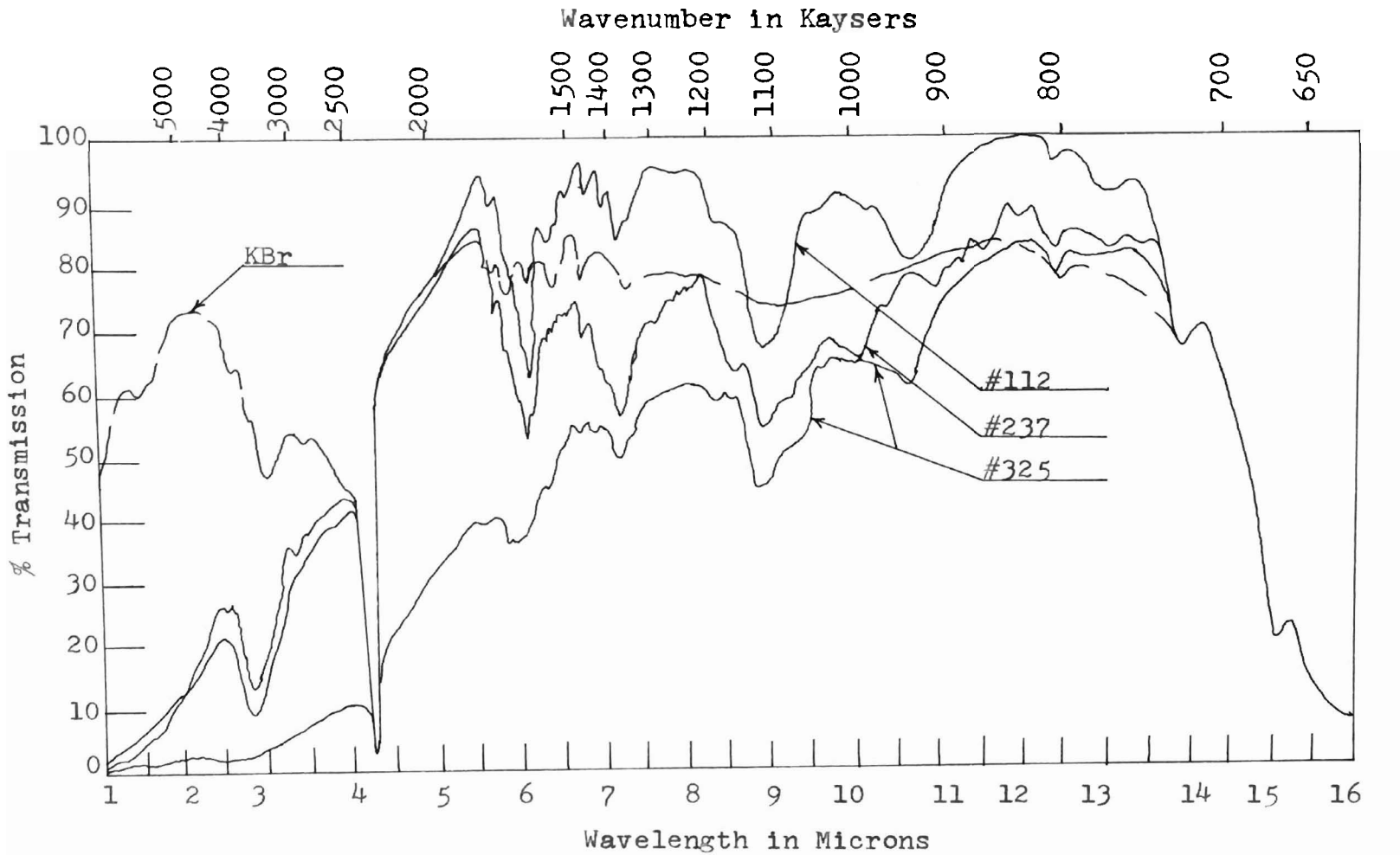

Figure 12. Infrared Spectra of Zinc Borates Heated at 800°C and KBr.

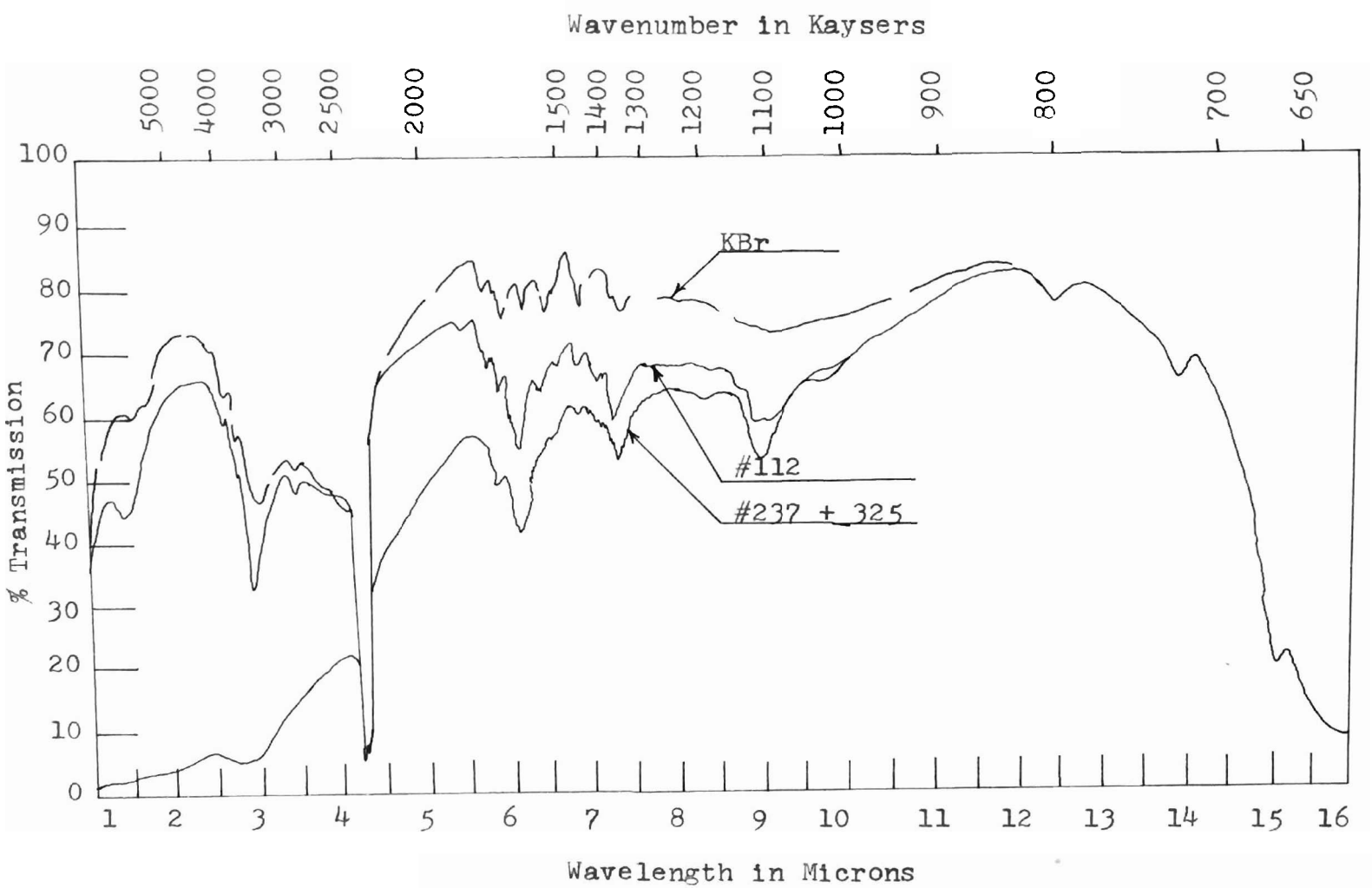

Figure 13. Infrared Spectra of Zinc Borates Heated at 1080°C and KBr.

illustrated that molecular ratios for ZnO/B_2O_3 of less than one were converted only to the cubic beta form. Molecular ratios for ZnO/B_2O_3 greater than one were shown to be converted at 600°C to the beta $ZnO \cdot B_2O_3$ form. However, molecules of alpha $5ZnO \cdot 2B_2O_3$ were also present in the system at temperatures past 600°C.

Sample #237 had a molecular ratio of 3:4 $ZnO:B_2O_3$ and had, therefore, only the beta form at temperatures greater than 600°C. Sample #325 had a molecular ratio of 4:3 $ZnO:B_2O_3$ and, therefore, had the beta form of $ZnO:B_2O_3$ and the alpha form of 5:2 $ZnO:B_2O_3$ at temperatures slightly in excess of 600°C.

Sample #112 had a molecular ratio of 1:1 $ZnO:B_2O_3$ (see Figure 8) which was exactly between the two phases indicated above (see Figure 8).

Figures 10 and 11 illustrated the transition from the alpha to the cubic beta form of the borates by the presence of new absorption peaks as the sample's temperature was increased from 585°C to 800°C.

Sample #112 and 325 showed identical absorption peaks at 800°C and sample #237 had absorption peaks which were in marked disagreement with samples #112 and 325. Very noticeable absorption peaks for samples #112 and 325 were present at 10.7 microns. Sample #237 showed no absorption peaks at this wavelength but showed a transmittance peak. Further-

more, sample #237 had three sharp absorption peaks between 11 and 12 microns. No absorption peaks were observed in this range for samples #112 and 325. Thus, from the data recorded in Figure 7, which assigned all zinc borates having a ZnO/B_2O_3 ratio of less than 1/1 a beta $ZnO \cdot B_2O_3$ structure, it was concluded that sample #237 had only the beta form.

Figure 7 also assigned an alpha $5ZnO \cdot 2B_2O_3$ and a beta $ZnO \cdot B_2O_3$ phase for a ZnO/B_2O_3 ratio of 4/3. Sample #325 was calculated to have an approximate 4:3 ratio of $ZnO:B_2O_3$ and exhibited infrared spectra different from sample #237. Therefore, the infrared data indicated without qualification that sample #325 had an alpha $5ZnO \cdot 2B_2O_3$ phase and a beta $ZnO \cdot B_2O_3$.

Infrared spectra analysis differentiated samples #237 and 325. Furthermore, it was concluded that sample #112 had both the beta $ZnO \cdot B_2O_3$ phase and the alpha $5ZnO \cdot 2B_2O_3$ phase present at temperatures in excess of 600°C as was indicated in Figure 7.

Figure 13 was obtained for the borates which were heated to temperatures in excess of their melting points or approximately 1100°C. When the samples were cooled a clear glass was formed. The glass was crushed and pulverized with KBr in a capsule. A short metal rod was placed in the capsule with the mixture and the capsule was vibrated at approximately 50 vibrations per second for one minute.

Figure 13 illustrated that all three glass borates gave the same spectra. The marked increase in absorption for samples #237 and 325 relative to sample #112 at wavelengths shorter than 8 microns was due to fogged pressed discs. Thus, as the wavelength approached the visible range of the spectrum the relative difference in absorption became more apparent.

Figure 14 was obtained from a comparison of an artificially prepared glass of ZnO and B_2O_3 which were present in the ratio of 3:2 respectively. The spectra obtained for the artificially prepared glass was identical to the glass spectra obtained for the three borates investigated in the study. Thus, Figure 14 gave a qualitative proof that the borate system studied was the ZnO-B_2O_3 system which existed in different ratios and gave identical glass infrared spectra.

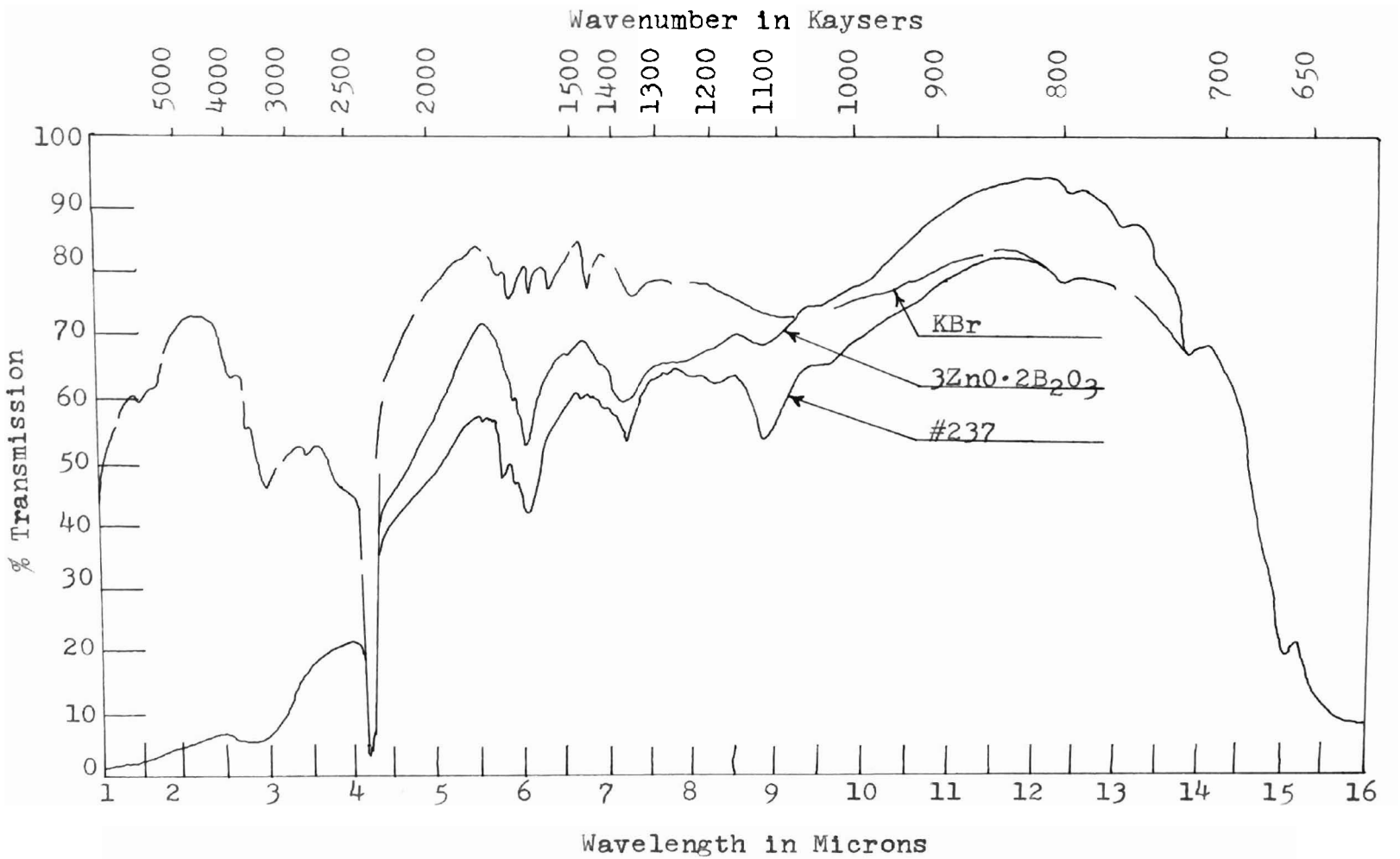

Figure 14. Infrared Spectra of an Artificially Prepared Glass of $3ZnO \cdot 2B_2O_3$, Glass from Sample #237, and KBr.

CHAPTER VII

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Summary and conclusions. The purpose of the study was to determine the composition of three hydrated zinc borates which were obtained from a commercial laboratory and to determine the number of hydrated water molecules associated with each borate.

A weight loss versus temperature study indicated that the borates did not lose their water of hydration in a "step-down" process. Hence the number of water molecules associated with each borate molecule were not determined by the number of such expected steps as was originally expected. A weight loss versus time study confirmed that the water of hydration was removed in a gradual process. Also, the borates lost their water of hydration at approximately the same rate. Total dehydration was achieved at 400°C.

Differential thermal analysis indicated a structural change occurring for all three borates as their temperature reached 600°C. The heat transformation at 600°C was shown to be exothermic from the differential thermal analysis data. Differential thermal analysis data also revealed the melting points of the borates which was indicated by an endothermic heat transformation at about 1000°C.

Refractive indexes of the zinc borate glasses proved

to be an unsuccessful means of determining the per cent composition of ZnO and B_2O_3 in the borates. Approximately identical refractive indexes were obtained for all glass borates.

A per cent composition of ZnO in the borates was done by classical volumetric analysis. The per cent B_2O_3 in each borate was obtained by subtracting the per cent ZnO and H_2O from 100 per cent.

Loss on drying indicated that the borates contained approximately .5 per cent absorbed water.

Molecular ratios of $ZnO:B_2O_3$ were obtained by plotting the per cent weight of ZnO against the corresponding molecular ratios. The molecular ratios for each borate were obtained for each borate by calculating the molecular ratio of ZnO/B_2O_3 which corresponded to the per cent composition of ZnO obtained from classical volumetric analysis. Samples #112, 237, and 325 had $ZnO:B_2O_3$ ratios of approximately 1:1, 3:4, and 4:3 respectively.

A table was made which indicated theoretical per cent loss for varying ratios of ZnO and B_2O_3 due to water of hydration. It was found that samples #112, 237, and 325 had approximately 3, 12, and 9 molecules of water respectively. This corresponded to 3 water molecules for each B_2O_3 group.

Infrared analysis confirmed the presence of a beta form present at a temperature in excess of 600°C. The

infrared spectra showed new absorption peaks for each borate whose temperature had been above 600°C.

Sample #112 and 325 had identical spectra and therefore had the same structure at temperatures in excess of 600°C. Sample #237 had different absorption peaks than samples #112 and 325 beyond 600°C.

Previous X-ray data by Harrison and Hummel had shown that borates which had molecular ratios less than $1ZnO/1B_2O_3$ converted to the cubic borate form at temperatures from 600 to 982°C. Thus, it was concluded that sample #237 had the beta form in this temperature range because it was shown to have a $ZnO:B_2O_3$ ratio of 3:4.

Molecular ratios of ZnO/B_2O_3 greater than 1/1 but less than 5/2 were shown to have the cubic beta form of $ZnO \cdot B_2O_3$ and an alpha form of $5ZnO \cdot 2B_2O_3$. Sample #325 had a ZnO/B_2O_3 ratio of about 4/3 and showed a different spectra than sample #237 at 800°C. Sample #112 had a spectrum identical to that of sample #325 at 800°C. Therefore, it was concluded that sample #112 had the same structure at 800°C as sample #325.

The borates formed a glass when heated to 1050°C and quenched in air. Infrared spectra for the three borates were identical which indicated identical structure for the borates when their temperatures were in excess of their melting points.

Recommendations. A study of the validity of refractive index of borates glasses as a means of per cent composition analysis should be done. Various glasses could be heated at temperatures in excess of the borate's melting points for increasing time periods to determine if the alpha to beta conversion was the factor affecting the refractive index measurements.

The infrared analysis should be further explored. Many artificial zinc borates differing only slightly in composition could be prepared and investigated in the infrared range to determine if the spectra was identical for all temperatures and molecular ratios within the phases determined by Harrison and Hummel whose graph was recorded as Figure 7.

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